

A NEW METHOD FOR GROWTH AND ANALYSIS OF NEXT-GENERATION IR DETECTOR MATERIALS

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ABSTRACT

This paper describes the development of a new analysis and crystal growth method for next generation infrared materials, namely, dilute nitride III-V semiconductors, which may be used in future low-cost night vision systems. The key to this method is isotopic enrichment of nitrogen-15 during material growth via molecular beam epitaxy, which allows enhanced detection of nitrogen using resonant nuclear reaction analysis. Films of GaAsN have been synthesized using nitrogen gas enriched in nitrogen-15, and examined using x-ray diffraction, secondary ion mass spectroscopy, and nuclear reaction analysis. This analysis has confirmed the incorporation of nitrogen-15 into the material corresponds with the expected enrichment of the feed gas, and opens up the possibility of examining the material using ion beam channeling methods to ascertain the lattice position of the incorporated nitrogen atoms.

1. INTRODUCTION

The Army's need for night-vision superiority is well known. To meet this need, the Army requires infrared (IR) detector materials with high detectivity that can be manufactured at low cost. Mercury Cadmium Telluride (MCT) is the current material technology of choice for performance reasons, but it is a II-VI material that has few other applications, can only be processed in dedicated fabrication facilities, and is therefore very costly. In contrast, III-V materials have many commercial and military applications, so an IR materials technology that can piggyback on the existing industrial III-V infrastructure would thus realize significant cost savings. Until recently there has not been a suitable III-V-based alternative to MCT, since the common III-V compounds cannot absorb in the long-wavelength band (8-12 micrometer) with the high quantum efficiency associated with direct bandgap materials like MCT. If one can develop a III-V direct bandgap material without intrinsic interfaces (as found in, e.g. Quantum Well Infrared

Photodetector (QWIP) or type II strained layer superlattices), we may realize the detectivity and durability needed for low-cost, high performance night vision system.

It has been theoretically predicted that the novel materials class labeled, dilute-nitrides, specifically the compound GaInSbN, can be lattice matched to GaSb and produce a direct band-gap material that can detect out to 20 micrometers, thus covering most tactical and strategic applications (Ashley, et al., 2003). Such materials would require the substitutional incorporation of 4-5% nitrogen into the group V sites of the semiconductor lattice. Until recently the highest concentration of nitrogen reported in GaSb_{1-x}N_x was 1.75% (Buckle, et al., 2005). Recent work at the Army Research Laboratory has doubled this to 3.5%, and there is no indication that a limit has been reached. However, at present, the optical quality of as-grown material is usually reduced, presumably because much of the nitrogen is incorporated at undesirable locations in the crystal lattice. In order to successfully further develop these materials, one must quantify both the concentration and location of the nitrogen atoms in the lattice.

At the Army Research Laboratory, the authors are developing a new crystal growth and analysis method, which combines two previously unrelated capabilities at two of ARL's research directorates, the Weapons & Materials Research Directorate (WMRD) and the Sensors & Electron Devices Directorate (SEDD). In previous work, researchers at WMRD showed that firing-induced nitrogen incorporation in gun barrel steel can have the beneficial effect of reducing the erosion of the barrel (Conroy, et al, 2004). A critical part of that project involved measuring the depth distribution of nitrogen under the surface of gun steels, using an ion beam analysis technique known as resonant nuclear reaction analysis (RNRA). In this method, a positive ion accelerator is used to direct a beam of light energetic ions onto a target material. A very small fraction of the

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incident ions will approach an atomic nucleus in the target material so directly that the strong nuclear forces which bind nuclei together can overcome the electromagnetic repulsion of the positively-charged ions and nuclei, and the two merge into a single, heavier atomic nucleus. Such "compound nuclei" are formed in highly excited states, and release that energy by either breaking apart into energetic particles, by releasing high-energy gamma rays, or both. For example, when a proton beam is directed onto a sample containing nitrogen, some protons and nuclei of a particular nitrogen isotope (^{15}N) combine to form excited ^{16}O nuclei, which almost immediately split apart (into ^{12}C and alpha particles), releasing a 4.43 MeV gamma ray. This characteristic gamma ray is a "fingerprint" for the presence of ^{15}N in the sample.

The sensitivity of NRA is limited by the natural abundance of the ^{15}N isotope, which is only 0.366% of natural nitrogen. When natural isotopic abundances of nitrogen are present, as in the case of gun barrel surface reactions, the uncertainty in the measurement (and the minimum detectable amount) is on the order of 0.3 atomic percent. In this work, molecular beam epitaxy is employed to grow GaInSbN films using isotopically enriched ^{15}N gas. Enriched nitrogen is commercially available in concentrations approaching 100% of the ^{15}N isotope, which means that the sensitivity of our RNRA measurements should be improved by more than two orders of magnitude over previous studies.

2. EXPERIMENTAL

Thin films of GaAsN were grown on GaAs substrates by molecular beam epitaxy (MBE), using a system equipped with a commercial nitrogen gas injector, which includes a unit that can form a plasma that produces energetic, single, N-atoms (nitrogen is otherwise always found in its molecular N_2 -state). The injector is fed gaseous nitrogen from one of two pressurized bottles containing either natural nitrogen gas (primarily ^{14}N) or nitrogen gas which has been enriched with the ^{15}N isotope.

The film growth started with the desorption of the oxide from the GaAs substrate surface by heating the sample wafer in an As flux to a specific temperature at which a regular reflection high-energy electron diffraction (RHEED) pattern is observed. The sample temperature was then lowered to a value suitable for growth of GaAs, and a 250-nm "buffer layer" of GaAs was deposited to produce material that was cleaner and had a smoother surface than the original substrate. Subsequently the temperature was lowered to a value that is suitable for growth of GaAsN, and the gas delivery line pressurized with enriched nitrogen gas. RF power was supplied to the plasma source and the mass flow controller (MFC) is set to a relatively large value that increases the background

pressure in the reactor to near $1\text{E-}5$ Torr. When the plasma strikes (visible light is observed), the MFC setting was immediately reduced to a value known to produce a stable reactor pressure. The system pressure and the plasma source were allowed to stabilize over a 40 minute wait period, after which the sample was exposed to molecular beams of Ga and As until a film approximately 200 nm thick was deposited. This was repeated using both the naturally-abundant nitrogen gas and the isotopically-enriched nitrogen gas.

The grown films of GaAsN and GaAs ^{15}N were then examined using secondary ion mass spectrometry (SIMS), x-ray diffraction, and resonant nuclear reaction analysis (RNRA). RNRA measurements were made using a 900 keV proton beam from a National Electrostatics 5SDH-2 positive ion accelerator. Characteristic gamma rays from the ($\text{p},^{15}\text{N}$) reaction were measured using a bismuth germanate scintillation detector.

3. RESULTS AND DISCUSSION

The successful incorporation of nitrogen into the growing GaAs film (i.e., GaAsN) is determined by recording an x-ray diffraction rocking curve as exemplified in Figure 1. The main peak at zero is a result of diffraction from the GaAs substrate, and the smaller peak at ~ 2100 arc sec is evidence of the GaAs ^{15}N film grown using isotopically-enriched ^{15}N gas. The many smaller peaks in between are Pendelloesung fringes whose presence indicate flatness of the film. Their frequency can furthermore be used to determine the thickness of the layer. The red curve is the theoretically-predicted signal from a GaAsN film given a film thickness of 193 nm and a N content of 3.9% of the Group V sites. The overall excellent agreement between the experimental (black) and theoretically predicted (red) curves is evidence for a very high-quality sample, equivalent to the crystalline quality of the GaAsN films that have grown using naturally-abundant nitrogen gas. The use of enriched gas had no apparent effect on the growth or quality of the resulting material.

To verify the incorporation of ^{15}N in the GaAs ^{15}N films, SIMS was performed on the same sample and a reference sample, which had been grown with natural nitrogen in an otherwise identical way (Figure 2). Note that because of the detectability limits of SIMS, the secondary ions actually measured are complexes of Ga and N, with total masses of 83 and 84 amu. The ratio of the intensity of these two signals yields the $^{15}\text{N}/^{14}\text{N}$ ratio in the materials. In the GaAsN grown with natural nitrogen gas, SIMS yields a $^{15}\text{N}/^{14}\text{N}$ ratio of 0.0037 – exactly as expected from natural nitrogen abundance. In the case of the film grown with enriched gas, this ratio is measured as ~ 55 , corresponding roughly to the expected enrichment of ^{15}N cited by the gas supplier ($\sim 98\%$).

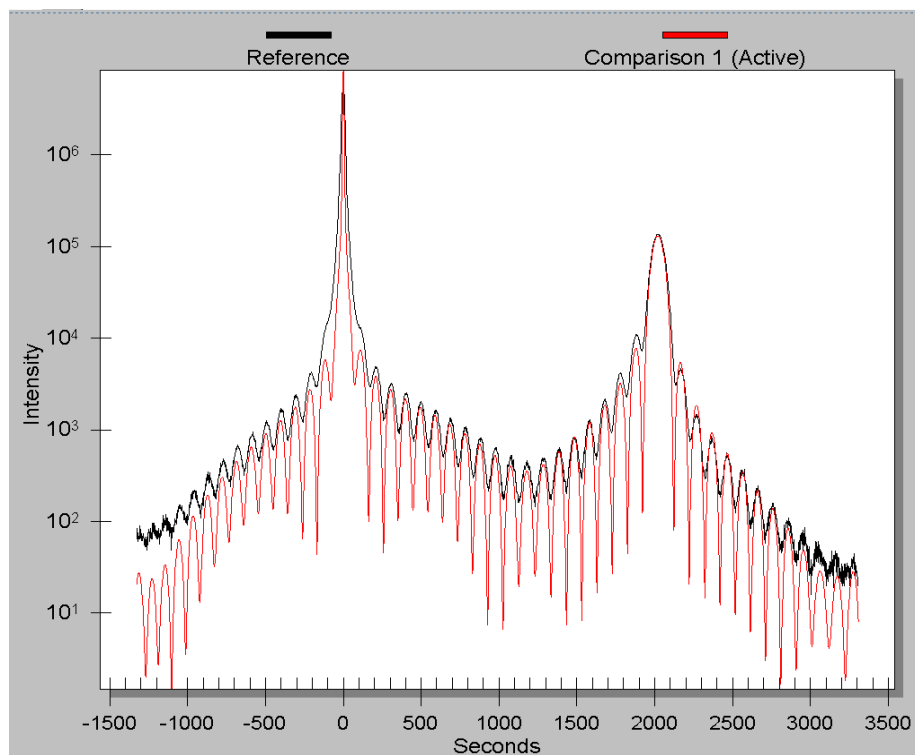


Figure 1. X-ray rocking curve from a $\text{GaAs}_{1-x}\text{N}_x$ film ($x=3.87\%$). The pronounced Pendelloesung fringes and overall good agreement between experiment (black) and theory (red) indicate excellent crystalline quality.

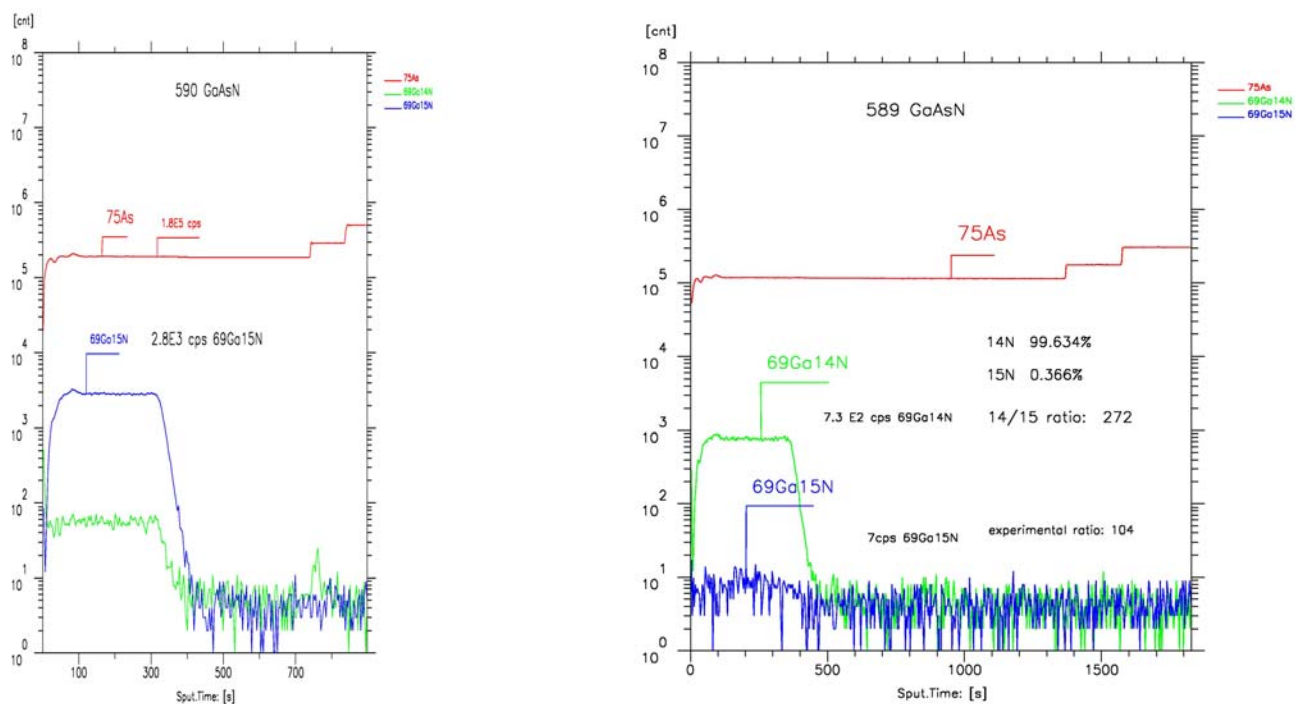


Figure 2. Secondary ion mass spectrometry (SIMS) profiles of GaAsN films grown with enriched ^{15}N gas (left) and naturally-abundant nitrogen gas (right).

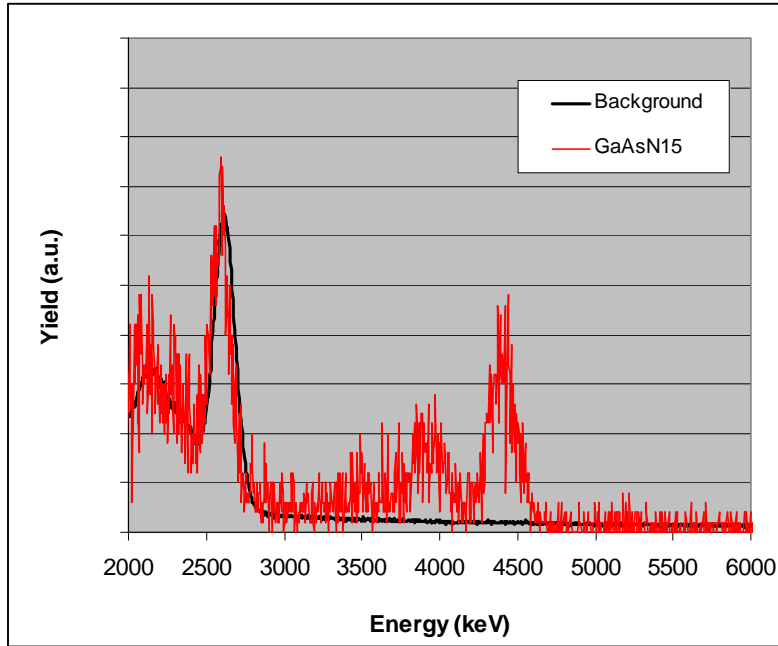


Figure 3. Gamma ray spectrum obtained using 900 keV protons incident on 200-nm thick GaAs¹⁵N.

The incorporation of the ¹⁵N isotope into the films was also confirmed using resonant nuclear reaction analysis (RNRA), as shown in Figure 3. The energy of the incident proton beam was adjusted to 900 keV so that protons would slow to the resonant reaction energy (897 keV) just beneath the surface of the material. At that energy, protons and ¹⁵N nuclei form a compound nucleus (¹⁶O) in a highly excited state, which almost immediately decays via the emission of an alpha particle into an excited ¹²C nucleus. This excited ¹²C transitions to its ground state via the emission of a gamma ray with an energy of 4.43 MeV. In Figure 3, this peak, and its associated first escape peak, is evident at 4.43 MeV and 3.92 MeV. The intensity of these peaks over the natural radioactivity background (cosmic rays and the thallium-208 gamma at 2.62 MeV) can be related to the actual concentration of ¹⁵N in the film, and studies are currently underway to quantify these results.

In more recent studies, the authors have begun to investigate the actual structure of the GaAsN films using a combination of RNRA and “ion beam channeling” techniques. In these measurements, currently underway, the single-crystal target is aligned with the incident proton beam using a precision goniometer and gamma ray yields are measured as the sample is brought in and out of alignment. If the incorporated nitrogen occupies substitutional sites in the III-V crystal structure – as desired for optimal effect on the bandgap of the material – the aligned planes and axes of the material will block the proton beam from interaction with the ¹⁵N nuclei when the sample is perfectly aligned, and resulting in a large reduction in gamma ray yield. If however the nitrogen

atoms are merely occupying interstitial sites in the lattice, contributing only unwanted optical scattering and decreased photoluminescence, then this alignment procedure will not result in such a large decrease in gamma ray yield (Spryutte et al, 2001). Identification of the actual lattice position of the incorporated nitrogen is a key factor in the development of these materials, and will guide MBE growth parameters, post-deposition treatments, and eventual optimization of these IR detector materials.

CONCLUSIONS

The growth of dilute nitride semiconductors using isotopically-enriched nitrogen gas has been demonstrated in GaAsN using MBE. The crystalline quality of the films was high, and not affected by the use of enriched gas. The incorporation of ¹⁵N into the grown material was confirmed using SIMS and resonant nuclear reaction analysis (RNRA). The isotopic enrichment in the semiconductor material results in high gamma ray yields, and will allow the future optimization of dilute nitrides using RNRA and ion beam channeling.

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REFERENCES

- T. Ashley, T. M. Burke, G. J. Pryce, A. R. Adams, A. Andreev, B. N. Murdin, E. P. O'Reilly and C. R. Pidgeon, 2003: InSb_{1-x}N_x growth and devices, *Solid-State Electronics*, **47**(3), 387-394.
- L. Buckle, B.R. Bennett, S. Jollands, T.D. Veal, N.R. Wilson, B.N. Murdin, C.F. McConville and T. Ashley, 2005: Growth of dilute GaNSb by plasma-assisted MBE, *Journal of Crystal Growth*, **278**(1-4), 188-192.
- Paul Conroy, Charles Leveritt, James Hirvonen and John Demaree, 2004: The Role of Nitrogen in Gun Tube Wear and Erosion" *Proceedings of the 24th Army Science Conference*, November 2004.
- Sylvia G. Spruytte, Christopher W. Coldren, James S. Harris, William Wampler, Peter Krispin and Klaus Ploog, 2001: Incorporation of nitrogen in nitride-arsenides: Origin of improved luminescence efficiency after anneal, *Journal of Applied Physics*, **89**(8), 4401-4406.